

2011 Minerals Yearbook

ARSENIC

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By George M. Bedinger

Domestic tables were prepared by Samir Hakim, statistical assistant, and the world production table was prepared by Lisa D. Miller, international data coordinator.

In 2011, the United States produced no arsenic and relied mainly on Morocco and China, the leading and second ranked import sources, respectively, for arsenic trioxide and on China for arsenic metal. There has been no domestic production of arsenic trioxide nor commercial-grade arsenic metal since 1985 following the closure of the ASARCO Incorporated copper smelter in Tacoma, WA. Arsenic trioxide was used mostly for the production of chromated copper arsenate (CCA), a pesticide and preservative used to pressure treat some wood products, and for production of agricultural chemicals; however, at yearend 2003, manufacturers voluntarily discontinued its use as a preservative for outdoor domestic wood products in residential applications, such as decks. Arsenic metal was used for electronics applications and in nonferrous alloys.

Legislation and Government Programs

In 1975, the Safe Drinking Water Act mandated that the U.S. Environmental Protection Agency (EPA) identify and regulate drinking water contaminants, including arsenic, that may have adverse effects on human health. The maximum contaminant level for arsenic was established at 50 parts per billion (ppb) and in 2001, was revised to 10 ppb.

In 2001, the EPA announced an initiative for research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the 2001 standards, provide technical assistance, and reduce compliance costs. Between July 2003 and July 2011, the EPA conducted 50 demonstration projects on treatment systems removing arsenic from drinking water in 26 States. The technologies used included adsorptive media (AM), iron removal (IR), coagulation/filtration (CF), ion exchange (IX), reverse osmosis, point-of-use, and system/process modification. A major objective of the demonstration program was to determine the cost-effectiveness of the technologies by collecting cost data associated with the 50 systems to include capital investment costs, site engineering, installation, and operation and maintenance (O&M) costs. The study found that capital investment costs for smaller AM, IR, and CF systems, with a design flowrate of less than 100 gallons per minute (gpm), varied extensively. The AM systems had higher O&M costs than IR, CF, or IX systems, owing mainly to media replacement costs. Based on average weekly labor hours reported, the AM systems required the least amount of time to operate and maintain (Wang and Chen, 2011, p. iv-vii, 1).

On December 16, the EPA issued the Mercury and Air Toxics Standards (MATS) to reduce emissions of toxic air pollutants from new and existing coal and oil-fired electric utility steam-generating units. MATS was designed to reduce emissions of heavy metals including arsenic, chromium, mercury, and nickel, and acid gases, including hydrochloric acid and hydrofluoric acid. The EPA

estimated that about 1,400 domestic coal- and oil-fired units would be affected. Existing plants have up to 4 years to comply with MATS (U.S. Environmental Protection Agency, 2011b).

Environmental and Human Health Issues

Arsenic is a naturally occurring element that may be present in drinking water as a result of weathering of arsenic-containing minerals exposed by natural processes or released by mining and smelting; as runoff from arsenic-containing pesticides used in orchards; in wastewater runoff from glass and electronics production; as arsenic released from coal-fired powerplants or underground coal fires; or from volcanic eruptions. In humans, some of the noncancerous effects of arsenic exposure include blindness, diarrhea, discoloration and thickening of the skin, nausea, stomach pain, and vomiting. Prolonged arsenic exposure has been linked to cancer of the bladder, kidney, liver, lungs, and prostate (Agency for Toxic Substances and Disease Registry, 2007, p. 1–30).

In December, the U.S. Food and Drug Administration (FDA) announced the results of the latest data collection of arsenic in apple juice. Analysis of 94 samples indicated that 95% of the samples tested below 10 ppb arsenic for total arsenic, and 100% below 10 ppb for inorganic arsenic, the carcinogenic form of arsenic. The FDA may set new guidance or a maximum level of arsenic concentrations for arsenic in apple juice and juice products in 2012 (U.S. Food and Drug Administration, 2011).

Researchers at the U.S. Geological Survey (USGS) released several studies regarding arsenic in groundwater. U.S. Geological Survey Scientific Investigations Report 2011–5013 assessed the concentration ranges of arsenic and uranium in bedrock wells with reference to the arsenic drinking water standard of 10 ppb that became effective in 2001. Data from 478 randomly selected wells indicated that 13% of the wells contained water with concentrations of arsenic greater than the standard (Colman, 2011, p. 1).

USGS Scientific Investigations Report 2011–5059 outlined a comprehensive analysis of data collected from monitoring drinking-water wells as part of the USGS National Water-Quality Assessment Program (NWQA). The study assessed arsenic occurrence and compared concentrations to human-health benchmarks for 24 trace elements, including arsenic. Seven percent of 5,097 wells tested exceeded the drinking water standard of 10 ppb for arsenic. The study also found that concentrations of arsenic were greater in drier regions and agricultural settings (Ayotte and others, 2011, p. 1).

Molycorp Inc. (Greenwood Village, CO) launched a proprietary rare-earth-based treatment technology in late 2010 that was effective at removing heavy metals such as arsenic, chromium, lead, mercury, and selenium from water. Molycorp identified four market areas for applications—municipal and

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industrial wastewater, recreational pools and spas, municipal drinking water, and consumer water purification (Molycorp Inc., 2012).

Researchers at Monmouth University (West Long Branch, NJ) devised a simple and inexpensive method to extract arsenic from drinking water. The process used pieces of plastic from used beverage bottles that were coated with cysteine, an amino acid. When placed in the water to be treated and circulated, the arsenic binds to the cysteine. Removing the cysteine-treated plastic after treatment resulted in water that met potable water standards for arsenic. Laboratory tests on water samples that originally contained 20 ppb arsenic produced water with 0.2 ppb arsenic or less (American Chemical Society, 2011).

Consumption

Apparent domestic consumption for arsenic, based on net imports, was about 4,910 metric tons (t) in 2011, a slight increase from 4,820 t in 2010. The estimated value of arsenic compounds and metal consumed domestically in 2011 was approximately \$5.4 million.

In June 2011, the U.S. Consumer Product Safety Commission, the U.S. Department of Agriculture, and the EPA published an interagency consumer awareness brochure for outdoor wooden structures that addressed how to determine whether a structure had been treated with CCA, the precautions necessary in using and maintaining treated wood, and proper disposal techniques. The residential use ban of CCA-treated wood at yearend 2003 did not require the removal of CCA-wood structures nor did it address the potential exposure to residues from existing structures (U.S. Consumer Product Safety Commission, 2011).

Domestic consumers of arsenic trioxide to produce CCA were Arch Chemicals, Inc., Norwalk, CT; Osmose Wood Preserving, Inc., Buffalo, NY; and Viance LLC, Charlotte, NC.

Arsenic metal was used, along with antimony, to harden ammunition, in solders, and in other applications. Grids and posts in lead-acid storage batteries are strengthened by the addition of arsenic metal. Arsenic is one of several metals used as an antifriction additive in babbitt metals (alloys that are used for bearings).

High-purity (99.9999%) arsenic metal was used to produce gallium-arsenide (GaAs), indium-arsenide (InAs), and indium-gallium-arsenide semiconductors that were widely used in computer, biomedical, communications, electronics, and photovoltaic applications. Arsenic may be used for germanium-arsenide-selenide or GaAs specialty optical materials.

The GaAs semiconductor market increased by 6% in 2011, a significant decrease from the 35% market growth in 2010. The decrease was attributed to weak demand for cellular telephones and wireless internet devices. In 2003, a standard cellular telephone typically contained less than 1 milligram of arsenic, contained in a single GaAs power amplifier. The adoption of sophisticated third-generation (3G) and fourth-generation (4G) smartphone handsets accelerated demand for GaAs power amplifiers. Fourth-generation smartphones use up to six times the amount of GaAs that a standard cellular telephone does (International Precious Metal Institute, 2003; Higham, 2012).

Prices

There was little change in the overall arsenic market and sales were low throughout 2011. According to U.S. Census Bureau data, prices of arsenic trioxide ranged between \$0.42 and \$0.51 per kilogram in 2011. Prices for 99%-pure arsenic metal in 2011 ranged from \$1,440 to \$1,550 per metric ton in January, increasing slightly to a range of \$1,550 to \$1,770 per ton by February, then decreased to a range of \$1,550 to \$1,720 per ton in August where they remained to yearend (Metal-Pages, 2012).

Foreign Trade

In 2011, domestic imports of arsenic compounds were 4,990 t contained arsenic, an overall increase of approximately 10% compared with the 4,530 t imported in 2010. Arsenic trioxide contains about 76% arsenic. In 2011, Morocco was the source of 71% of the arsenic trioxide imported into the United States, China was the source of 16%, and Belgium was the source of 12%.

In 2011, the United States imported 628 t of arsenic metal, an 18% decrease compared with the 769 t of arsenic metal imported in 2010. China was the leading source of arsenic metal in 2011 and provided 611 t of arsenic metal, or 97%.

Exports of arsenic metal from the United States in 2011 increased to 705 t from 481 t in 2010. Export destinations included Honduras (45%), France (31%), Guatemala (12%), and Colombia (8%). In the Harmonized Tariff Schedule (HTS), exported materials are classified only by HTS number and may or may not be inspected so as to confirm the contents of the shipping container. This may have resulted in misclassification of exported material, and therefore, actual exports of arsenic metal may be less than that reported. The exports may also include arsenic-containing electronic waste such as computers and other electronics destined for reclamation and recycling.

In June, the EPA hosted a workshop with the Materials Systems Laboratory (MSL) of the Massachusetts Institute of Technology (Cambridge, MA) and the National Center for Electronics Recycling (Parkersburg, WV) to improve information flows on e-waste exported from the United States and on the global movement of used electronics. Used electronics were frequently shipped from the United States to developing countries that lack the capability to appropriately handle the material and where they may be taken apart by hand to obtain valuable materials such as copper, silver, and gold. In the process, workers may be exposed to high levels of contaminants such as arsenic, cadmium, lead, and mercury. The workshop brought together stakeholders from academia and industry, government agencies, and international and nonprofit organizations to address the challenges associated with collecting data on used electronics transboundary movements. Participants in the workshop identified approaches useful in characterizing electronic waste exports from a qualitative and quantitative perspective. The summary report of the workshop was released in January 2012 (U.S. Environmental Protection Agency, 2011a; Miller and others, 2012, p. 88).

World Review

In 2011, commercial-grade arsenic trioxide was thought to have been recovered from processing of nonferrous ores or concentrates in nine countries. Reduction of arsenic trioxide to arsenic metal accounted for all world output of commercial-grade (99%-pure) arsenic metal. Arsenic-containing residues and smelter dusts recovered from nonferrous metals plants in several countries may not have been processed to recover commercial-grade arsenic trioxide in 2011 and may have been stockpiled for future treatment. Production data for most countries were estimated.

In 2011, China produced approximately 25,000 t of arsenic trioxide and remained the world's leading producer followed by Chile (10,000 t), and Morocco (8,000 t). In China, in addition to reclaiming arsenic as a byproduct of nonferrous smelting, arsenic was recovered as a byproduct of gold mining from orpiment (As2S3) and realgar (AsS), the more common ore minerals of arsenic (Peters and others, 2002, p. 182).

In April, BacTech Environmental Corp. (Toronto, Ontario, Canada) was awarded a contract by the Mines Branch of Manitoba Department of Innovation, Energy and Mines to remediate a stockpile of arsenopyrite concentrate in Snow Lake, Manitoba, Canada. BacTech planned to use its patented bioleaching technology that uses bacteria to oxidize sulfate compounds to treat the arsenic. The remediation would be no cost to the taxpayers because BacTech would recover a high percentage of the gold contained in the stockpile. The company planned to construct a bioleach plant to treat 37,500 t/yr of the stockpiled material; the project was estimated to last 5 to 6 years (BacTech Environmental Corp., 2011, p. 2–3).

Outlook

The voluntary decision by the wood preservative industry to eliminate CCA as a wood preservative for certain wood products has led to a decline in U.S. consumption and a decline in arsenic trioxide production in China. The use of alternative wood preservatives and wood alternatives, such as concrete, plastic, or wood composites, will continue to reduce use of CCA wood preservatives. Borate-treated wood is resistant to insects and fungal decay, but its use is recommended only for interior or weather-shielded applications. Specific industrial applications, such as marine timber, plywood roofing, and utility poles, are expected to continue to use CCA-treated wood.

World sources of arsenic, as arsenic trioxide and arsenic metal from nonferrous metal processing, are expected to be sufficient to meet projected needs.

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 $\label{eq:table 1} \textbf{TABLE 1} \\ \textbf{ARSENIC SUPPLY-DEMAND RELATIONSHIPS}^1$

(Metric tons of arsenic content)

	2007	2008	2009	2010	2011
U.S. supply, imports:					
Metal	759	376	438	769	628
Compounds	7,010	4,810	4,660	4,530	4,990
Total	7,770	5,180	5,100	5,300	5,620
Distribution of U.S. supply:					
Exports ²	2,490	1,050	354	481	705
Apparent consumption	5,280	4,130	4,740	4,820	4,910

¹Data are rounded to no more than three significant digits; may not add to totals shown.

 $\label{eq:table 2} \textbf{U.s. IMPORTS FOR CONSUMPTION OF ARSENIC PRODUCTS}^1$

	201	10	2011		
	Quantity	Value	Quantity	Value	
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)	
Arsenic trioxide:					
Belgium	973	\$603	794	\$458	
China	1,260	561	1,080	486	
Germany	4	29	(2)	3	
Japan			(2)	4	
Morocco	3,690	1,640	4,690	2,290	
Total	5,920	2,830	6,570	3,240	
Arsenic acid:					
Indonesia	20	8			
Japan	(2)	3	4	26	
Taiwan	40	32	20	17	
Total	60	43	24	42	
Arsenic sulfide, Russia	13	35	2	28	
Arsenic metal:					
China	639	1,020	611	999	
Finland			(2)	10	
Germany	1	297	2	407	
Japan	125	1,100	15	697	
Korea, Republic of	4	11			
United Kingdom	(2)	7	(2)	17	
Total	769	2,440	628	2,130	

⁻⁻ Zero

Source: U.S. Census Bureau.

²Metal only.

Data are rounded to no more than three significant digits; may not add to totals shown.

²Less than ½ unit.

 $\label{eq:table 3} \text{ARSENIC TRIOXIDE: ESTIMATED WORLD PRODUCTION, BY COUNTRY}^{1,2,3}$

(Metric tons)

Country ⁴	2007	2008	2009	2010	2011
Belgium	1,000	1,000	1,000	1,000	1,000
Bolivia ⁵		74	115	155	150
Chile	11,400	10,000	11,000	11,000	10,000
China	25,000	25,000	25,000	25,000	25,000
Iran	100	100	100	100	100
Japan	40	40	40	40	40
Kazakhstan	r, 5	r, 5	r	^r	
Mexico	1,600	513	500		
Morocco	8,950 5	8,800	8,500	8,000	8,000
Peru ⁶	4,321 5	4,822 5	301 ^r		
Portugal	15	15	15	15	15
Russia	1,500	1,500	1,500	1,500	1,500
Total	53,900 ^r	51,900 ^r	48,100 ^r	46,800 ^r	45,800

Revised. -- Zero.

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¹Including calculated arsenic trioxide equivalent of output of elemental arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production.

²World totals and estimated data have been rounded to no more than three significant digits; may not add to totals shown.

³Table includes data available through March 28, 2012.

⁴Austria, Hungary, the Republic of Korea, Serbia and Montenegro, South Africa, Ukraine, the United Kingdom, and Zimbabwe have produced arsenic and (or) arsenic compounds in previous years, but information is inadequate to make estimates of output levels, if any.

⁵Reported figure.

⁶Output of Empresa Minera del Centro del Perú (Centromín Perú) as reported by the Ministerio de Energía y Minas.